

Production of γ -valerolactone from lignocellulosic biomass for sustainable fuels and chemicals supply



Xing Tang^a, Xianhai Zeng^a, Zheng Li^a, Lei Hu^b, Yong Sun^{a,*}, Shijie Liu^c, Tingzhou Lei^d, Lu Lin^{a,*}

^a College of Energy, Xiamen University, Xiamen 361005, China

^b Jiangsu Key Laboratory for Biomass-based Energy and Enzyme Technology, Huaiyin Normal University, Huai'an 223300, China

^c College of Environmental Science and Forestry, State University of New York, 1 Forestry Drive, Syracuse, NY 13210, USA

^d Henan Academy of Sciences, Zhengzhou, China

ARTICLE INFO

Article history:

Received 20 April 2014

Received in revised form

20 July 2014

Accepted 30 July 2014

Keywords:

γ -Valerolactone

Platform chemical

Biofuels

Heterogeneous catalytic systems

Biomass

ABSTRACT

Recently, valorization of lignocellulosic biomass, the most abundantly available biomass raw material on the Earth, to biofuels and chemicals has attracted great attention worldwide for the purpose of reducing our overwhelming reliance on the non-renewable petroleum resources. γ -Valerolactone (GVL) has recently been hailed as a versatile building block which can be derived from renewable lignocellulosic biomass resource for energy, chemical and material sectors. In this review, focus was principally put on the applications of GVL as a renewable carbon source for green solvents and transportation fuels. In addition, advances in the GVL production through selective reduction of commercial or biomass-derived levulinic acid (LA) and its esters using various hydrogen sources, mainly including molecule H₂, formic acid (FA) and alcohols, have been carefully summarized. Moreover, assessment of the relative merits of different hydrogen sources for the GVL production has also been performed.

© 2014 Elsevier Ltd. All rights reserved.

Contents

1. Introduction.....	608
2. Employing GVL as a solvent	609
3. GVL and its derivatives as fuel	610
4. The production of GVL from commercial/biomass-derived LA	612
4.1. Using external molecular H ₂ as hydrogen source	612
4.2. Using formic acid (FA) as hydrogen resource	615
4.3. Using alcohols as H-donors.....	616
5. Summary and outlook.....	617
Acknowledgments.....	617
References	617

1. Introduction

Our society relies heavily on non-renewable fossil resources to produce liquid fuels and chemicals, which were consumed to improve the quality of people's lives and drive global economy forward. However, depleting fossil-based resources alongside

environmental deterioration compels us to seek renewable and clean resources for the sustainable supply of fuels and chemicals. Biomass is defined as all plant and plant-derived materials including starch, sugar, oil crops and animal manure, which is the only current renewable resources on the Earth that can be converted to liquid fuels and chemicals to replace fossil-derived counterparts [1]. Small or no additional CO₂ emission occurs during the production and utilization of bioenergy, easing or even eliminating negative impact on the carbon balance of our biosphere [2]. The estimated biomass production in the world is

* Corresponding authors. Tel.: +86 592 5952786; fax: +86 592 5952786.

E-mail addresses: sunyong@xmu.edu.cn (Y. Sun), lulin@xmu.edu.cn (L. Lin).

1.70×10^{11} t per year by biosynthesis and composed of roughly 75% carbohydrates [3]. In the United States, the annual dry biomass potential is over 1.3×10^{10} t which can be used to produce biofuels to replace more than 30% of the country's current petroleum consumption [1]. It is also expected that bioenergy supplies 15% of global primary energy by 2050 [4,5]. Recently, scientists have put a lot of efforts to produce fuels and chemicals from biomass by chemcatalytic conversion routes or direct liquefaction which possess the advantage of high process efficiency as compared with conventional biological process [6–8]. For example, fuel ethanol is one of the present dominated commodities produced by the fermentation of biomass (mainly starch) in an industrial-scale which could be added into the regular gasoline to reduce the consumption of fossil resources in the U.S. and Brazil or elsewhere [9]. However, the current fuel ethanol industry is limited by its potential threat to food security and the “blend-wall” issues [10–12]. In this context, valorization of lignocellulosic biomass, the most abundantly available biomass resource, to “drop-in” biofuels is a better alternative avenue to ease our overwhelming dependence on nonrenewable fossil resources [13]. Such drop-in biofuels could directly be shipped into the existing fuel infrastructure without any changes as petroleum products, thus avoiding the requirement of special facilities for blending with regular gasoline. Converting lignocellulosic biomass to platform chemicals is envisaged as a key step to realize the above fascinating prospect. Biomass-derived platform chemicals, such as levulinic acid (LA) [14], 5-hydroxymethyl (HMF) [15,16], furfural [17] and γ -valerolactone (GVL) [18], retain moderate functionalities to ensure the required stability for storage and transportation and the essential reactivity for upgrading to other chemicals and fuels as compared with that of carbohydrate.

Recently, GVL has been hailed as a versatile biomass-derived platform molecule that can be used as a renewable carbon source for the production of liquid fuels and chemicals. Physicochemical properties of GVL were listed in Table 1. Many research efforts have recently been paid to the conversion of lignocellulosic biomass to GVL. It is well-known that lignocellulose consists of cellulose (~45% of dry weight), hemicellulose (~30% of dry weight) and lignin (~25% of dry weight) [11]. Both cellulose and hemicellulose fractions could be used as the starting materials to produce GVL (Fig. 1). Cellulose, a polysaccharide consisting of a linear chain of β -glycosidic bonds linked D-glucose units, could be degraded to glucose through chemical or enzymatic catalytic hydrolysis [19], and the isomerization of the resulting glucose to fructose would take place in the presence of acid catalysts [20]. Then, the dehydration of the latter occurred to form HMF (3 in Fig. 1), followed by rehydrating to LA (4 in Fig. 1) [20]. HMF and LA

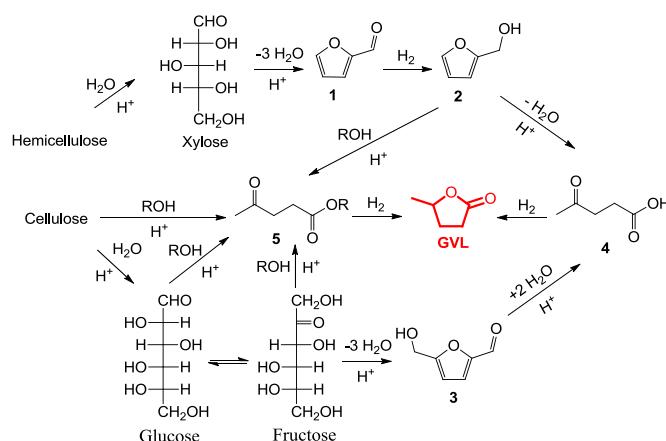


Fig. 1. The reaction pathways for the production of GVL from cellulose and hemicellulose.

are also identified as useful biomass-derived platform molecules for producing liquid fuels and carbon-based chemicals from lignocellulosic materials [15,21]. In addition, cellulose or carbohydrates could be directly converted into alkyl levulimates (5 in Fig. 1) through alcoholysis in alcohols [22–26]. Finally, LA and its esters could be selectively reduced to GVL over various heterogeneous or homogeneous catalytic systems. As for hemicellulose (composing primarily of the pentose sugars), xylose is one of the main hydrolysates originating from hemicellulose and could be firstly degraded to furfural (1 in Fig. 1) catalyzed by mineral acid or solid acid [27]. The resulting furfural could be converted to furfuryl alcohol (FAL, 2 in Fig. 1) by catalytic hydrogenation [28], followed by the hydrolysis or alcoholysis of FAL to yield LA or its esters respectively [29–32]. Hence, LA and its esters could be produced from either cellulose or hemicellulose fraction though cascade reactions, and were subjected to the subsequent hydrogenation to GVL. In this review, advances in GVL production via selective reduction of commercial or biomass-derived LA and its esters using various hydrogen sources, mainly including molecule H₂, formic acid (FA) and alcohols, have been systematically summarized. In addition, we also mainly emphasize here on employing GVL as a green solvent for biomass conversion and employing GVL as a precursor for the production of transport fuels.

2. Employing GVL as a solvent

Horváth et al. [18] have firstly proposed that GVL is a promising sustainable liquid from biomass for the production of other carbon-based chemicals, because GVL has many advantages of renewability, non-toxicity, stability and biodegradability. Fegyvernek et al. [37] have also synthesized and characterized several GVL-derived chemicals that could be used as outstanding green solvents, including alkyl 4-alkoxyvalerate and GVL-derived ionic liquids. Recently, Strádi et al. [38] have surveyed the hydrogenation of olefins in GVL-based ionic liquids to obtain alkanes. The turnover frequency of the catalysts in GVL-based ionic liquids was found to be significantly higher than that in regular ionic liquids such as 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and the hydrogenation reaction was also found to be highly selective to the C=C double bonds even in the presence of other unsaturated functional groups.

Interestingly, GVL itself is also an excellent solvent for the transformation of biomass into chemicals and fuels. Recently, Duan et al. [39] have reported that the synthesis of phosphatidylserine, a significant ingredient in functional food and pharmaceutical industries [40], was conducted with a 95% yield using GVL as

Table 1
Physicochemical properties of GVL [18,33–36].

Property	Value
CAS-No	108–29–2
Formula	C ₅ H ₈ O ₂
MW (g/mol)	100.112
Refractive index (n _{20/D})	1.432
Density (g/mL)	1.05
Flash Point (°C)	96
Melting point (°C)	−31
Boiling point (°C)	207–208
Solubility in water (%)	100
LD ₅₀ , oral for rat (mg/Kg)	8800
Kinematic viscosity (mm ² /s) (40 °C)	2.1
ΔH _{vap} (kJ/mol)	54.8 ± 0.4
Δ _c H° _{liquid} (kJ/mol)	−2649.6 ± 0.8
ΔH° ₂₉₈ (kJ/mol)	−461.3
Cetane number	< 10
Lower heating value (MJ/kg)	25

solvent. Qi et al. [41] have demonstrated catalytic conversion of fructose, glucose and sucrose to HMF and LA in GVL/H₂O mixture solution by tandem processes. Poor solubility of fructose in pure GVL (0.01 g/100 g GVL) was observed, which would be improved moderately by adding H₂O and H₂SO₄. The maximum HMF yield of around 75% and LA yields ranged from 50% to 70% were obtained on the basis of the diversity of carbohydrates under the optimal reaction conditions. The resulting LA could be converted in-situ to GVL with a yield of 55% (based on fructose) using FA as hydrogen source in the presence of Shvo catalyst [42]. This catalytic strategy eliminates the separation of LA and opens a promising door to employ GVL as a solvent for the conversion of biomass to platform chemicals.

Dumesic and co-workers have developed a biphasic system consisting of GVL and aqueous HCl solution saturated with NaCl to produce LA from cellulose [43]. The majority of LA (greater than 75%) derived from the degradation of cellulose in aqueous HCl solution shifted to GVL phase, facilitating a LA yield as high as 72%. Dumesic et al. have also tried to hydrogenate the resulting cellulose-derived LA to GVL over Ru-Sn/C in GVL phase. GVL and soluble humins were found having negative impact on the catalyst and resulted in a considerable decrease in the rate of LA conversion. Interestingly, all products formed by cellulose deconstruction are solubilized by GVL, avoiding the trouble of pipeline plugging usually caused by insoluble humins in a monophase system (aqueous). The dissolved humins could be precipitated and separated from GVL by dilution with a mass of water followed by filtration. However, the concentration and purification of LA and GVL from the resulting diluent must be an energy-intensive process, because significant quantities of water must be removed by distillation.

The conversion of biomass to platform chemicals over heterogeneous catalysts is highly desirable, because heterogeneous catalysts can be easily separated and recovered from the reaction system. Unfortunately, poor water-solubility of biomass materials (such as cellulose) leads to a weak interaction between solid acid catalysts and feedstock in water, resulting in a poor LA yield but a high selectivity to by-products (humins). Alonso et al. [44] found that cellulose could be completely dissolved in GVL/H₂O solution under the applied reaction conditions, improving its accessibility to active sites on the surface of solid catalysts. When the conversion of cellulose to LA was conducted in GVL/H₂O (9/1, w/w), LA yield as high as 69% was achieved using Amberlyst 70 as the catalyst, in contrast, only a low LA yield of 20% was obtained in water under the same conditions. Apparently, the good solubility of cellulose in GVL/H₂O mixture solution should be mainly responsible for this high LA yield over solid acid catalysts.

Converting hemicellulose to furfural has also greatly promoted when GVL was used as the solvent. Gurbuz et al. [45] have recently demonstrated that the conversion of xylose into furfural with a high furfural yield of 81% at 175 °C using solid acid catalyst in GVL/H₂O (9/1, w/w). In contrast to net water reaction system, side-reactions between furfural and active intermediates derived from xylose were suppressed in GVL/H₂O (9/1, w/w) system, namely, furfural was stable with a high yield in this GVL/H₂O system. Most importantly, Gurbuz et al. found that C6-sugars (glucose and fructose) could degraded into furfural replacing HMF or LA as the main product in GVL/H₂O solution. The furfural yield of 32% and 36% were obtained starting from glucose and fructose, respectively, which were the highest yield of furfural from hexose so far. But the mechanism of hexose to furfural is not very clear now and further study is essential to get more insight into this transformation. Zhang et al. [46] have also employed GVL as solvent to produce furfural from xylose, xylan and corncob catalyzed by FeCl₃·6H₂O. A surprisingly high furfural yield of 79.6% from untreated corncob was achieved at 185 °C for 100 min

in GVL/H₂O solution. Apparently, one can inferred that a fraction of cellulose in corncob was also converted to furfural in GVL/H₂O solution. In view of exceptional performance of GVL as solvent, Alonso and co-workers have recently developed an attractive strategy for the conversion of cellulose and hemicellulose simultaneously into LA and furfural respectively, giving high yields in a single reactor using sulfuric acid as catalyst in GVL/H₂O (9/1, w/w) solution [47]. The results suggested that a long retention time and high acid concentration lead to more furfural degradation, but facilitate the LA accumulation. Thus, varying reaction times and acid concentrations could selectively switched products between LA and furfural. This solvent system could be applied to the conversion of lignocellulosic biomass materials comprising of different cellulose and hemicellulose fractions into LA and/or furfural with high yields, respectively. Take corn stover for example, LA yield of 58% and furfural yield of 67% were achieved under the optimal reaction conditions. As compared with LA, furfural could be easily recovered from the reaction system by distillation as its high volatility, preventing the further degradation of furfural. Furfural could also be converted to LA by consecutive hydrogenation and hydrolysis processes (Fig. 1), followed by the reduction of the resulting LA to yield GVL in the GVL solvent. Lignin fraction and humins were dissolved into GVL and hindered greatly the subsequent selective hydrogenation of LA over solid catalysts. Although, lignin and solid humins could be precipitated from GVL by dilution with a mass of water and then be removed by filtration, the concentration of the resulting diluent to remove water is an energy-intensive process.

Recently, a nonenzymatic sugar production approach was successfully developed using lignocellulosic materials (corn stover, hard wood and softwood) in a solvent mixture of GVL, H₂O and dilute sulfuric acid [48]. In this report, Luterbacher and co-workers demonstrated that biomass feedstock was charged into a packed-bed flow-through reactor, and solvent was flowed through the biomass at a constant rate, while the reactor was heated from 430 K to 490 K with a prescribed linear temperature ramp. High yields of soluble carbohydrates ranged from 70% to 90% were obtained on the basis of the source of feedstock (corn stover, maple wood and loblolly pine). Aqueous phase enriched with the resulting carbohydrates was separated from GVL by liquid CO₂ extraction [49]. The separated carbohydrates could further be upgraded to furans (HMF and furfural) by chemcatalytic process with a desirable yield or to ethanol by fermentation at high titers. As compared with H₂O or ethanol/H₂O solution, GVL/H₂O solution reported here exhibited unparalleled performance for the deconstruction of lignocellulosic materials into soluble carbohydrates. The role of GVL for the increased deconstruction of biomass can be ascribed to complete solubilization of lignocellulosic materials in GVL/H₂O solution and disruption of cellulose crystallinity by GVL, greatly improving accessibility to feedstock surface. In addition, GVL also has the potential to be used as the suitable solvent for the valorization of lignin or humins into high-valued chemicals and fuels because of favorable solubility of lignin and humins in GVL [5,50], but a few studies are concentrated on this issue to date.

3. GVL and its derivatives as fuel

Recently, GVL is considered as a new renewable liquid for gasoline and diesel fuel oxygenate. Horváth et al. have concluded that GVL is a better alternative than ethanol as a fuel additive due to its lower vapor pressure and relatively higher energy content [18]. GVL does not form an azeotrope with water as compared with ethanol, which resulted in an energy-intensive concentration process to remove water during ethanol production by fermentation. Bruno et al. [51] have systematically characterized the

mixtures of 91 AI summer quarter gasoline and GVL using the Advanced Distillation Curve methodology. The addition of GVL led to the distillation curve to lower temperatures for diesel fuel, but to higher temperatures for gasoline. The addition of GVL also significantly facilitated to reduce the concentration of CO and smoke in automobile exhaust [36], but phase separation appeared when high concentration of GVL was added.

It is noted that some defects of high water solubility, smaller cetane number, and relatively lower energy density as compared with fossil-based fuels limit the application of GVL in the transportation sector (Table 1). In order to overcome above-mentioned weaknesses of GVL, increasing attentions have recently been paid to upgrade GVL to “true” liquid fuels by catalytic hydrogenolysis/hydrogenation. Methyl tetrahydrofuran (MTHF) formed by catalytic hydrogenolysis of GVL is also regarded as a promising biofuel [18,52–54], because it could be blended up to 70% in gasoline and has an high octane number of 87 [6]. Lange et al. have also demonstrated a valeric biofuel strategy starting from cellulose that cellulose-derived GVL could converted into valeric acid though the ring opening and hydrogenation over Pt-zeolite followed by esterification of valeric acid to valerates as fuel additives (Fig. 2) [55–59]. Compared with ethanol, butanol and MTHF, valerates have a higher energy content and suitable polarity paralleled to conventional fuels. Moreover, the volatility-ignition properties of different valerates could be regulated by tuning their alkyl chain length to meet the requirement to be used as gasoline or diesel oxygenates. For example, regular gasoline blended with ethyl valerate (EV) at 10 and 20 vol% still met the specification of European gasoline; however, heavier esters such as pentyl valerate (PV) were more suitable to be used as diesel due to its better volatility and cold-flow property. More practically, Lange et al. evaluated the performance of regular gasoline blended with 15 vol% EV by a road trial based on ten vehicles with a cumulative

distance of 250, 000 km. No measurable impact on engine wear, oil degradation, vehicle durability, engine deposits, or regulated tailpipe emissions was observed when EV was added into gasoline. Compared with the strategy reported by Lange et al., Chan-Thaw et al. [60] recently described a one-pot approach to produce EV and PV with a high of 70% over inexpensive Cu/SiZr.

However, it is infeasible to employ either MTHF or valerates to completely replace petroleum fuels in the transportation sector due to their relatively lower energy densities. Recently, Dumesic and co-workers have developed two attractive catalytic strategies for the conversion of GVL into liquid alkenes that can be directly used as transportation fuels [61,62]. In the first catalytic strategy (Fig. 3), GVL in the aqueous firstly underwent ring opening to an isomeric mixture of unsaturated pentenoic acids, followed by decarboxylation to produce butene isomers with equimolar quantities of CO_2 . Dumesic et al. demonstrated that both of these transformations could be proceeded over $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst at elevated pressures in a fixed bed reactor (Fig. 3, Reactor 1) [63–65], and the butene yield as high as 98% was achieved under the optimal reaction conditions. The resulting butene in gas stream could be selectively converted to liquid C_{8+} alkenes in the presence of CO_2 through oligomerization over solid acid catalysts (HZSM-5 or Amberlyst 10) in the second fixed bed reactor (Fig. 3, Reactor 2). Low molecular weight alkenes was also formed via cracking, but C_{8+} alkenes was the desired products that can be directly employed as jet fuel. In integrated catalytic system consisting of two flow reactors, the selectivity to C_{8+} alkenes from GVL was reached 77% under the optimal conditions. Noble metal catalysts and external hydrogen source were not required in this integrated system reported by Dumesic et al., minimizing production costs of alkene fuels from GVL. Further techno-economic analysis for this integrated catalytic strategy was also conducted and Dumesic et al. declared that the production of liquid fuels via this approach was superior to a lignocellulosic ethanol production strategy reported by NREL economically [66].

In the second catalytic strategy (Fig. 4), GVL could be upgraded to C_9 alkenes by progressive deoxygenation. Serrano-Ruiz et al. have recently developed a catalytic route for the conversion of GVL into 5-nonenone by cascade reactions in two continuous flow

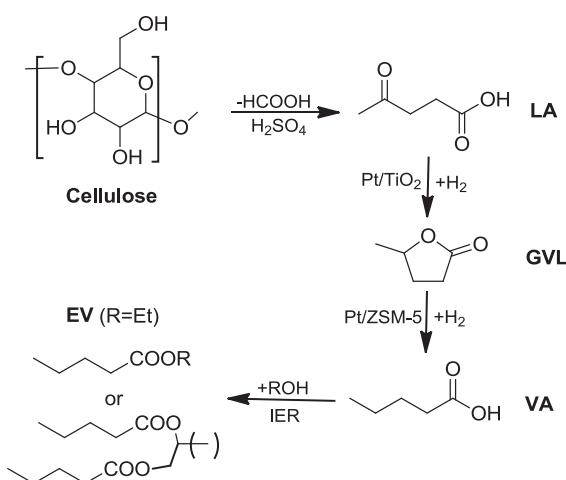


Fig. 2. Proposed pathway for the conversion of cellulose to valeric biofuels [55].

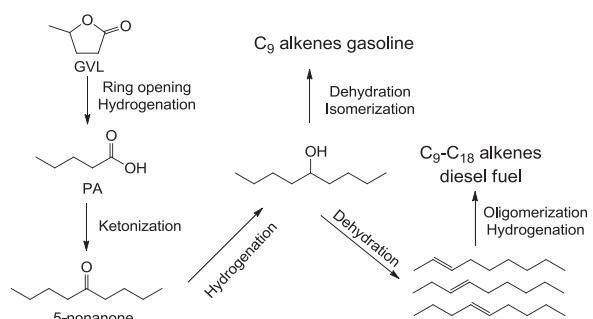


Fig. 4. The reaction pathways for conversion of GVL to $\text{C}_9\text{--C}_{18}$ alkene fuels [61].

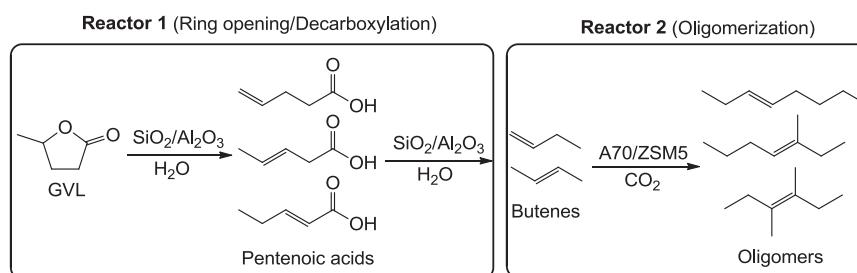


Fig. 3. The reaction pathways for conversion of GVL to butenes and liquid alkene fuels [62].

reactors [67,68]. Firstly, a synthetic aqueous streams of GVL (50 wt%) with H₂ was fed into a fixed bed reactor loaded with Pd/Nb₂O₅ catalyst and the carbon selectivity toward pentanoic acid (PA) as high as 92% was achieved by the ring opening of GVL in the presence of H₂SO₄. Pd/Nb₂O₅ provided good hydrothermal stability and sulfur resistance property to ensure the ring-opening of GVL to PA under mineral acid and water environments. The resulting stream containing PA was consecutively fed into the second reactor charged with Ce_{0.5}Zr_{0.5}O₂ catalyst and the carbon selectivity of 84% toward 5-nonenone was obtained [67,69]. Techno-economic analysis for the production of 5-nonenone from LA was also estimated as well [70]. Subsequently, 5-nonenone could be reduced to 5-nonenol over Ru/C catalysts. The latter underwent dehydration and isomerization over USY zeolite catalyst to produce a mixture of branched C₉ alkenes with appropriate performances for the application in the transportation sector [61,68].

In addition to being used as solvent or precursor for liquid fuels, GVL is also widely employed in flavoring industry [71] and organic synthesis field [72–75], or used as feedstock for the formation of valeric acid [76,77], 1,4-pentanediol [52,78–80], amino compounds [81] and so on (Fig. 5). Interestingly, Zhao et al. [82] have recently reported that the conversion of GVL into aromatic hydrocarbons through catalytic pyrolysis over various zeolites. Some research efforts have also been paid to convert GVL into monomers of polymer materials, and the resulting composites show outstanding thermostability, mainly attributing to robust five-membered ring structure originating from GVL [83–86].

GVL is recently identified as a renewable carbon source for the sustainable supply of chemicals, liquid fuels and polymer materials, however, the future role of GVL will strongly depend on its manufacturing costs from biomass. Therefore, more attentions should be paid to reduce the production cost of GVL from biomass resources through effective catalytic conversion routes.

4. The production of GVL from commercial/biomass-derived LA

Generally, GVL directly formed via selective hydrogenation of commercial/biomass-derived LA under external hydrogen sources using various catalysts. In this review, advances in the production of GVL from commercial/biomass-derived LA via multiple catalytic systems have been detailedly summarized on the basis of the diversity of hydrogen sources. We mainly concentrate on the usage of external molecule H₂, formic acid (FA) and alcohols as hydrogen

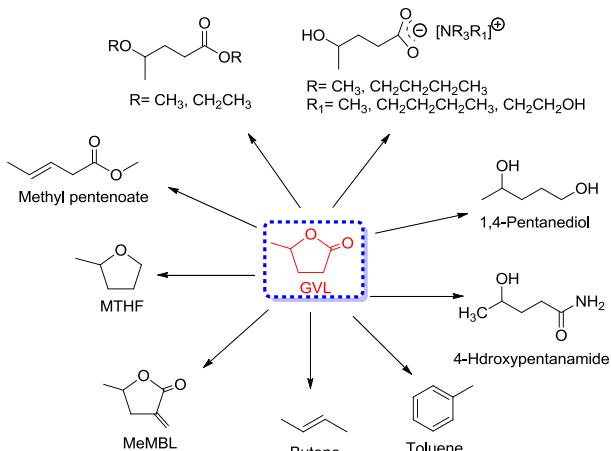


Fig. 5. The pathways for the conversion of GVL into other chemicals.

sources and also assessed the relative merits of different hydrogen sources for the GVL production.

The probable selective hydrogenation pathway of LA to GVL is shown in Fig. 6. In a liquid-phase hydrogenation route, 4-hydroxypentanoic acid (HPA) is confirmed as the intermediate through hydrogenation of the carbonyl group at C4 position of LA using various homogeneous or heterogeneous catalysts [87–89]. HPA is regarded as a thermolabile compound which is rapidly converted to GVL via lactonization in the presence of acid catalysts [90]. In a gas-phase hydrogenation route, LA is prone to form α-angelica lactone (AAL) via enolization under elevated-temperature and the resulting AAL is subsequently reduced to the desired product GVL using H₂ and catalysts [91,92].

4.1. Using external molecular H₂ as hydrogen source

Molecular H₂ is the most common hydrogen source for the reduction of unsaturated organic compounds due to its easy-separable feature in liquid reaction systems. Recently, various catalytic hydrogenation systems for GVL production have been successfully developed using commercial/biomass-derived LA and external molecular H₂ as hydrogen source.

Homogeneous catalytic systems for the hydrogenation of LA to GVL are summarized in Table 2. The story of homogeneous catalytic systems for GVL production could be traced back to 1991. Braca et al. [93] reported the conversion of carbohydrate-derived LA to GVL in the presence of ruthenium iodocarbonyl (Ru(CO)₄I₂) with HI or NaI as co-catalyst, and the overall GVL yield of 39.5% was obtained starting from glucose. Starodubtseva et al. [94] demonstrated a Ru^{II}-BINAP-HCl catalytic system in which ethyl levulinate (EL) was converted to GVL with a yield of 95%. This catalytic system was also efficient (85% GVL yield) even under a very mild condition of 25 °C and 18 h. Ru(acac)₃ with different ligands was also employed as catalysts for the selective reduction of LA, the maximum GVL yield of 95% or 100% was obtained in aqueous solution or solvent-free conditions, respectively [95]. Further, Kühn et al. have investigated the effect of various water soluble phosphine ligands on the catalytic activity of Ru species [96], indicating active Ru species were unstable at the absence of ligands under the applied reaction conditions. The significant role of phosphine ligands was also demonstrated by Tukacs and co-workers [97]. Biphasic system consisting of dichloromethane and water was also reported for the hydrogenation of LA to GVL using a water-soluble Ru-(TPPTS) catalyst [88]. After reaction, GVL and Ru-based catalyst dissolved into organic and aqueous phases respectively, facilitating the recycle of catalysts. Besides Ru-based catalysts, Ir was also employed as the active metal for the hydrogenation of LA, achieving a high yield with TONs as high as 78,000 [98,99]. Compared with heterogeneous catalytic system, homogeneous catalytic system has a remarkable advantage in high TONs because of strong interaction between substrates and homogeneous catalysts. However, complicated expensive ligands

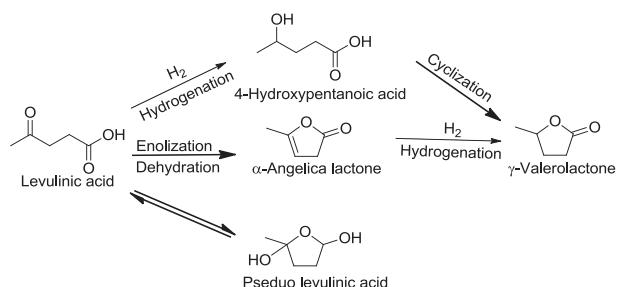


Fig. 6. The probable mechanism for selective hydrogenation of LA to GVL.

Table 2Representative of homogeneous systems for the production of GVL from LA using external H₂.

Catalyst	Solvent	P (bar)	T (°C)	t (h)	Yield (%)	Reference
Ru(CO) ₄ I ₂	Water	100	150	8	87	[93]
Ru ^{II} -BINAP	Ethanol	60	60	5	95	[94]
Ru(acac) ₃ +TPPTS	Water	69	140	12	95	[95]
Ru(acac) ₃ +PBu ₃ +NH ₄ PF ₆	No	100	135	8	100	
RuCl ₃ +TPPTS	Dichloromethane/water	45	90	1.3	100	[88]
Ru(acac) ₃ +PTA	Water	50	140	5	3	[96]
Ru(acac) ₃ +TXXTPS	Water	50	140	5	21.85	
Ru(acac) ₃ +TPPMS	Water	50	140	5	88.36	
Ru(acac) ₃ +TPPTS	Water	50	140	5	96.03	
Ru(acac) ₃	Water	50	140	5	98	
Ir(CO) ₂ Cl ₂ +KOH	Ethanol	50	100	15	96	[98]
Cp [*] Ir(H ₂ O)(4,4-diOMe-2,2-diPy)	Water	10	120	4	98	[99]
Ru(acac) ₃ +Bu-DPPDS	No	10	140	4.5	99.9	[97]
Ru(acac) ₃ +Pr-DPPDS	No	10	140	4.5	98.9	

and poor recoverability of homogeneous catalysts limit its applications in a commercial scale for GVL production.

Given the above-mentioned shortcoming of homogeneous systems, heterogeneous catalytic systems containing effective recyclable supported catalysts are highly desirable for the hydrogenation of LA to GVL. Recently, many research efforts have been paid to employ heterogeneous catalytic systems for the selective hydrogenation of LA using external molecular H₂ and the corresponding advances are summarized in Table 3.

The earliest records of heterogeneous catalytic systems for hydrogenating LA could be date back to 1930s [100]. The best GVL yield of 87% was achieved under room temperature with a duration of 44 h using H₂ (2.3–3.0 bar) and PtO₂. Raney Ni was also used as the catalyst for reduction of LA with approximately GVL yield of 90% under elevated temperature and H₂ pressure [78,101]. Later in the 1950 s, Dunlop and Madden [102] have reported an effective gas-phase hydrogenation approach to produce GVL in a fixed bed reactor loaded with reduced CuO/Cr₂O₃ catalyst, giving a maximum GVL yield of 100% at 200 °C with feed rates of 1.2 g/min (LA) and 5 L/min (H₂). Broadbent et al. [103] have also demonstrated that a moderate GVL yield of 71% was obtained under solvent-free condition with H₂ pressure of 150 bar over Re₂O₇. Recently, Ru-Ni supported on ordered mesoporous carbon was prepared for the solvent-free hydrogenation of LA and gave an optimal GVL yield of 97% [104]. The excellent catalytic activity of this bimetallic catalyst was ascribed to the homogeneous embedding of Ru-Ni bimetallics in mesoporous carbonaceous matrix with strong metal-support interaction.

Several noble-metal-free catalysts consisting of Cu/Cr/Fe/Ni were also employed for the hydrogenation of LA to GVL [105–108]. For instance, Hengne and co-workers [109] have accomplished a quantitative conversion of LA to GVL over nanocomposites of Cu-ZrO₂ and Cu-Al₂O₃ in aqueous phase. Hengne et al. believed that acidity of the supports of ZrO₂ and Al₂O₃ facilitated the dehydration of the intermediate 4-HPA to aim GVL. GVL yields of above 90% were obtained over these inexpensive catalysts, although severe reaction conditions involving high temperatures (> 200 °C) and H₂ pressure were required. Recently, Ni-MoO_x/C bimetallic catalyst was prepared and gave a maximum GVL yield of 97% under solvent-free and mild reaction conditions (8 bar H₂, 140 °C, 5 h) [110]. The better catalytic performance of Ni-MoO_x/C as compared with other noble-metal-free catalysts was attributed to the co-presence of metallic Ni and partially reduced MoO₂ species. Reduced Co₃O₄ also showed a favorable activity and stability for hydrogenating EL to GVL under a relatively reaction conditions [111].

Precious metal catalysts were confirmed having sufficient catalytic activity ensuring the hydrogenation of LA under relatively

mild conditions. To date, Ru/Ir-based supported catalysts have been verified as most active catalysts for the reduction of LA to GVL in heterogeneous catalytic systems. Manzer et al. [84] concluded firstly that 5% Ru/C showed more catalytic activity as compared with other activated carbon supported catalysts (like 5% Pt/C) for the hydrogenation of LA to GVL. The GVL yield was peaked at 97% under a moderate conditions of 150 °C and 500 psig H₂ over 4 h. Lin and co-workers [87] obtained the same conclusion in methanol media under milder reaction conditions than that Manzer applied. Ru/C catalyst also showed outstanding catalytic performance for gas hydrogenation of LA as compared with Pt, Pd and Ni-based catalysts [91,112,113]. The excellent performance of Ru-based catalysts is partially attributed to the nature of the supports. Al-Shaal et al. [114] also found that the catalytic activity of Ru/C was much higher than Ru/Al₂O₃ and Ru/SiO₂, for the selective reduction of LA and its esters to GVL. The GVL yield of 97.5% was achieved over Ru/C at room temperature under H₂ pressure of 12 bar for 50 h, in contrast, GVL yields of only 1.7% and 6.3% were recorded over Ru/SiO₂ and Ru/Al₂O₃ respectively. The dispersion of Ru nanoparticles (Ru-NPs) supported on activated carbon, a key parameter to control catalytic activity of the supported catalysts, was much better than that of supported on other supports. For instance, the dispersion of Ru-NPs supported on TiO₂ could be improved by lowering the loadings of active metal from 5% to 0.6%, resulting in a higher GVL yield of 93% over 0.6% Ru/TiO₂ than that over 5% Ru/C (90%) at the same reaction conditions [115]. Besides the dispersion of active metal, water was also proven to be responsible for the outstanding activity of Ru-based catalysts in aqueous phase because the calculated energetic barrier of the reaction pathway was decreased in the presence of H₂O [116]. Recently, García et al. have reported the reduction of LA to GVL over in-situ generated Ru-NPs with size of 2–3 nm, resulting in a high GVL yield of 99% at 130 °C for 24 h under 25 bar H₂ in water [117]. But, the catalytic activity of these in-situ generated Ru-NPs was decreased significantly after only three consecutive run. In addition, Pd-NPs were also prepared and employed as the catalyst for the selective hydrogenation of LA [118,119]. Compared with Ru-NPs, relatively tougher reaction conditions (180 °C, 6 h and 90 bar H₂) were the prerequisite to ensure a high GVL yield using Pd-NPs.

Some efforts have recently been paid to produce GVL under very mild conditions in order to improve the economy of heterogeneous hydrogenation systems. The presence of acid co-catalysts was confirmed to be largely promoted the hydrogenation of LA to GVL under very mild reaction conditions using Ru/C catalyst. For example, GVL yield of 99.9% was readily obtained using Ru/C and Amberlyst 70 as co-catalyst at 70 °C, 0.5 MPa H₂ for 3 h in water [120]. However, the LA conversion of only 13% was measured in

Table 3Representative of heterogeneous systems for the production of GVL from LA using external H₂.

Catalyst	Solvent	P (bar)	T (°C)	t (h)	Yield (%)	Reference
5 wt% Ir/C	1,4-Dioxane	55	150	2	47	[84]
5 wt% Ru/C	1,4-Dioxane	55	150	2	72	
5 wt% Ru/SiO ₂	Water/scCO ₂	100	200		99	[49]
316 SS + HOTf	Water	55.2	75	24	100	[126]
Ru-NPs	Water	5	130	12	100	[117]
CuO/Cr ₂ O ₃	Water	70	200	10	90.7	[106]
Cu/Al hydrotalcite	Water	70	200	10	85.8	[107]
CuO/CuFe ₂ O ₄	Water	70	200	10	90.1	[105]
Ni-Cu/Al ₂ O ₃	Water	65	250	2	96	[108]
5 wt% Pd/SiO ₂	Water	90	180	6	96.5	[118]
5 wt% Pd/MCM-41	Water	60	240	10	96.3	[119]
5 wt% Cu/ZrO ₂	Water	35	200	5	100	[109]
0.64 wt% Ru/TiO ₂	Water	35	150		93	[115]
5 wt% Ru/C+A70	Water	3	70	3	99.9	[120]
5 wt% Ru/H _{PA}	Water	5	70	4	99	[122]
2 wt% Ru/SPES	Water	30	70	2	87.9	[125]
Ru@DOWEX	Water	5	70	7	99.8	[127]
4.5 wt% Ir/CNT	Water	20	50	1	99	[121]
PtO ₂	Ethanol	2.3–3	22–24	44	87	[100]
Ru/C	Methanol	12	130	2.5	92	[87]
5 wt% Cu/ZrO ₂	Methanol	35	200	5	90	[109]
Reduced CuO/Cr ₂ O ₃	Vapor phase	0.07–0.35	200		100	[102]
5 wt% Cu/SiO ₂	Vapor phase	10	265		99.9	[54]
5 wt% Ru/C	Vapor phase	1	265		98.6	[91]
5 wt% Pd/C	Vapor phase	1	265		90	
30 wt% Ni/HZSM-5	Vapor phase	1	250		92.2	[112]
30 wt% Ni/SiO ₂	Vapor phase	1	250		87	[113]
Raney Ni	No	62	185	4.5	93	[101]
5 wt% Ru/C	No	12	25	50	97.5	[114]
Ru-NPs	No	12	130	24	95	[117]
1 wt% Ru/TiO ₂	No	40	200	10	97.5	[129]
1 wt% Ru/H-β	No	40	200	4	91.0	
0.3 wt% Ru/OMC	No	45	150	2	97	[104]
Ni-MoO _x /C	No	8	140	5	97	[110]
RuSn(3.6:1)/C	SBP	35	180	overnight	97	[131]

the absence of acid co-catalyst under the same reaction conditions. Besides Ru-based catalysts, iridium nanoparticles supported on carbon nanotubes (Ir/CNT) was also showed an unexpected activity under mild reaction conditions. A high GVL yield of 99% was achieved over Ir/CNT at 50 °C, 2 Mpa H₂ for only 1 h in water, and a GVL yield of 97% was also obtained even under solvent-free conditions over 20 h [121]. It is noted that LA could be completely converted even in presence of formic acid (FA, co-produced with LA in an equimolar amount during the acid hydrolysis of lignocellulosic biomass) using Ir/CNT catalyst in aqueous phase. Therefore, biomass-derived LA/FA stream may be used directly as the feed for the production of GVL. But, Ir is also one of noble metals and much more expensive than Ru.

Acidic co-catalysts and supports, including trifluoromethanesulfonic acid (HOTf), hydroxyapatite, polyethersulfone, H-ZSM5 and H-β, have been proven to catalyze the lactonization of intermediates HPA to GVL under mild reaction conditions, thus facilitating the holistic conversion of LA into GVL [122–128]. For example, LA could be completely converted to GVL catalyzed by 316 stainless steel with the assistance of HOTf at 75 °C [126]. However, acidic supports would further catalyzed the ring-opening of the resulting GVL to form over-reductive compounds, including PA, pentenoic acid, 1,4-pentanediol and MTHF, at higher reaction temperatures (> 200 °C) [129].

Multiphase systems have also been developed to promote the separation of desired products and catalysts from the reaction solvent. Bourne et al. [49] have developed an attracting biphasic catalytic system consisting of supercritical CO₂ (scCO₂, the upper) and water (the lower) for the synthesis of GVL. LA was hydrogenated to GVL with a yield of 99% catalyzed by Ru/SiO₂ in water, and the resulting GVL would transfer spontaneously to scCO₂

phase from aqueous phase. Almost pure GVL was obtained after separation and pressure-relieving of supercritical CO₂. It is noted that high pressure (10 MPa) was the prerequisite for the formation of scCO₂/H₂O biphasic system. A liquid triphase system (aqueous phase/ionic liquid/organic phase) was also demonstrated for the recovery of catalysts after reaction [130]. In this triphase catalytic system, Ru/C or a homogeneous Ru precursor was dispersed in ionic liquid phase before and after reaction, and could be easily separated from reaction mixture for the next test. A high selectivity of 100% toward the desired product was achieved at 100 °C under 35 bar H₂ for 4 h, however, the cost of ionic liquid limited its applications in a commercial scale. Furthermore, Dumesic et al. have reported a water/2-sec-butyl-phenol (SBP) biphasic system for selective hydrogenation of LA using RuSn bimetallic catalysts [131]. The high partition coefficient of GVL between SBP and water was ensured the extraction of GVL from water to SBP phase. SBP was regarded as a renewable solvent which could be produce from lignin [132]. However, the doping of Sn avoided the formation of hydrogenated products from solvent as compared with monometallic Ru/C catalyst under the applied reaction conditions.

The conversion of biomass-derived LA directly into GVL is highly desirable due to the elimination of costly separation of LA, largely facilitating the economy of GVL production from biomass. Heeres et al. [133] have recently reported a one-pot process for GVL production from fructose using trifluoroacetic acid (TFA) and Ru/C as the catalysts for dehydration and subsequent hydrogenation, respectively. A maximum GVL yield of 62% based on fructose was obtained under the optimal conditions (180 °C, 94 bar H₂, 8 h). Similarly, one-pot conversion of cellulose to GVL was also reported using niobium-based solid acids and Ru/C as the catalysts for the LA production and the subsequent hydrogenation,

respectively [134]. Recently, a two-steps approach was successfully developed for the conversion of giant reed to GVL under mild conditions [135]. Giant reed was firstly treated in 0.4 M HCl solution at 180 °C for 1 h to produce LA with a yield of 59.1% (based on cellulose fraction). After neutralization and filtration, the biomass-derived LA was directly hydrogenated to GVL over Ru/C with niobium oxide or niobium phosphate as co-catalysts. This approach gave a GVL yield of 16.6 wt% (calculated on giant reed starting weight) at 70 °C under 3 MPa H₂ for 5 h. Additionally, FAL derived from hemicellulose is an alternative to be used as feedstock for the production of GVL (Fig. 1). Hengne et al. [136] have demonstrated a two steps-“one pot” approach by which FAL was firstly converted to methyl levulinate (ML) using sulfonic acid functionized ionic liquids and the resulting ML was subsequently reduced to GVL over Ru/C. Sulfonic acid functionized ionic liquid ([BMIm-SH][HSO₄]) was found having little impact on the Ru/C catalyst, and the maximum GVL yield of 68% starting from FAL was achieved in methanol.

4.2. Using formic acid (FA) as hydrogen resource

Formic acid has recently been regarded as a promising hydrogen source and hydrogen storage material [137,138]. Depending on the reaction mechanism previously reported, FA formed in an equimolar amount with LA through acidic hydrolysis of carbohydrates [20,139,140]. Employing FA as in situ hydrogen source for the selective hydrogenation of biomass-derived LA embodies the principle of atom economy (Table 4). Recently, Horváth et al. have demonstrated a homogeneous catalytic system to convert LA to GVL by hydride transfer from HCOONa using $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{bpy})(\text{H}_2\text{O})]\text{[SO}_4]$ in an acid aqueous solution (pH=4) [95]. This catalytic systems gave a GVL yield of only 25% at 70 °C for 18 h under N₂, and over-reduced product 1,4-pentandiol (25%) was also detected by GC-MS analysis. Inexpensive sulfate was also used as a temperature-switchable base for the transfer hydrogenation of LA from FA under hydrothermal conditions, but a maximum GVL yield of only 11.0% was obtained in the presence of Na₂SO₄ for 12 h [141].

FA can also be decomposed into molecular H₂ and CO₂ for the hydrogenation of LA over metal catalysts. Heeres et al. have described a one-pot catalytic route that fructose was converted to GVL by cascade reactions in the presence of trifluoroacetic acid (TFA) and Ru/C using external FA as hydrogen source [133]. It is noted that both of the decomposition of FA and the hydrogenation of LA were catalyzed by Ru/C. The highest GVL yield of 52% was

obtained starting from fructose at 180 °C, 16 h and 50 bar N₂. In situ generated Ru-NPs were also showed an attracting catalytic activity for the transformation of synthetic LA/FA stream into GVL. This in situ catalyst gave a completely quantitative conversion of LA at 130 °C for 24 h with the assistance of Et₃N [117]. Nevertheless, a poor stability of these Ru-NPs was observed after only three consecutive run. Recently, Ag–Ni–ZrO₂ nanocomposite was prepared for the hydrogenation of LA using FA as hydrogen source. LA with equimolar amount of FA was quantitatively converted to GVL in aqueous at 220 °C for 5 h over Ag–Ni–ZrO₂, in contrast, GVL yield of only 22% or 34% was achieved over Ag/ZrO₂ or Ni/ZrO₂ respectively [142]. The exceptionally performance of Ag–Ni–ZrO₂ nanocomposite was attributed to the surface synergism between Ag and Ni.

Shvo catalyst was also developed to hydrogenate LA to GVL using FA as a in situ hydrogen source under solvent-free conditions [42]. Shvo catalyst is an effective catalyst for the decomposition of FA into CO₂ and H₂ [149], however, the presence of CO₂ largely hindered the subsequent hydrogenation of LA [148]. It is noted that Shvo catalyst is also very expensive and difficult to be recycled from the reaction system.

It is practically significant to convert biomass-derived LA/FA, rather than synthetic LA/FA, to GVL. Fu et al. have recently developed an efficient homogeneous catalytic system that biomass-derived LA/FA was directly converted to GVL in the presence of RuCl₃/PPh₃ and bases co-catalysts [143]. The activity of Ru-based complex catalyst was closely associated with the intensity of bases co-catalysts (Basicity: KOH > NaOH > NEt₃ > pyridine > NH₃ > LiOH). The overall GVL yield of 48% based on glucose was achieved at 150 °C for 12 h in the presence of RuCl₃/PPh₃ and pyridine, and no extra H₂ or FA was added into this reaction system. However, poor water resistance of this Ru-based complex catalyst was observed and the recovery of spent catalyst from this homogeneous catalytic system was also very difficult. In view of above-mentioned disadvantages of homogeneous catalytic system, a two-step process has been developed for the conversion of LA to GVL using FA as hydrogen source over immobilized Ru catalyst (Ru-P/SiO₂) and Ru/TiO₂ [144]. Catalysts could be readily recovered from the solvent after reaction, although, a considerable decrease in hydrogenation rate of LA was observed using this heterogeneous catalytic system as compared with previous homogeneous system. Most importantly, it is difficult to hydrogenate biomass-derived LA over Ru-P/SiO₂ catalyst due to the presence of humins.

Table 4
Representative of catalytic systems for the production of GVL from LA using FA.

Catalyst	Source of LA/FA	T (°C)	t (h)	Yield (%)	Reference
$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{bpy})(\text{H}_2\text{O})]\text{[SO}_4]$	Synthetic	70	18	25	[95]
Na ₂ SO ₄	Synthetic	220	12	11.0	[141]
Ru-NPs+Et ₃ N	Synthetic	130	24	100	[117]
Ag–Ni–ZrO ₂	Synthetic	220	5	99	[142]
Ag-ZrO ₂	Synthetic	220	5	22	
Ni-ZrO ₂	Synthetic	220	5	34	
RuCl ₃ /PPh ₃ +Et ₃ N	Synthetic	150	12	90	[143]
RuCl ₃ /PPh ₃ +pyridine	Synthetic	150	12	88	
Ru-P/SiO ₂ +Ru/TiO ₂	Synthetic	150	6	30	[144]
Au/ZrO ₂	Synthetic	150	6	99	[145]
Ru/C	Synthetic	150	5	90	[146]
RuCl ₃ /PPh ₃ +pyridine	Glucose	150	12	48	[143]
Cu/ZrO ₂	Synthetic	200	5	100	[147]
Shvo catalyst	Synthetic	95	6	99.9	[148]
Ru/C	Fructose/external	180	16	52 ^a	[133]
Au/ZrO ₂	Glucose	150	8	51 ^a	[145]
Au/ZrO ₂	Cellulose	150	8	33 ^a	[145]
Cu/ZrO ₂	Giant reed	200	12	18.5 (wt%) ^a	[147]

^a Based on the carbohydrates or biomass.

Cao et al. have demonstrated a fascinating hydrogen-independent catalytic strategy for transferring biomass-derived LA/FA into GVL over Au/ZrO₂ [145,146,150]. Au/ZrO₂ catalyst showed unparalleled performance that FA could be completely decomposed into H₂ and CO₂ at 150 °C for only 20 min. Prolonging reaction duration to 6 h, GVL yield of 99% was easily achieved from LA with equimolar amount of FA over Au/ZrO₂ in aqueous. When aqueous solution containing biomass-derived LA and FA (partially neutralized to pH=2) was used as feed, the overall GVL yield of 51% or 33% was obtained over Au/ZrO₂ starting from glucose or cellulose, respectively. These results indicate that Au/ZrO₂ catalysts have outstanding water resistance and high catalytic activity even in the presence of intractable humins. Au is an expensive and rare metal on the earth, therefore, Cu/ZrO₂ catalyst was also prepared for the hydrogenation of LA using FA as hydrogen source [147]. Compared with Au/ZrO₂, relatively tough reaction conditions were essential to ensure a high GVL yield over Cu/ZrO₂ catalyst. For example, synthetic LA/FA stream could be completely converted to GVL over Cu/ZrO₂ at 200 °C under 1 MPa N₂ for 5 h. Cu/ZrO₂ catalyst gave a highest GVL yield of 18.5 wt% from giant reed-derived LA/FA stream (partially neutralized to pH=2) at 200 °C under 1 MPa N₂ for 12 h.

4.3. Using alcohols as H-donors

Aldehyde or ketones can be reduced to corresponding alcohols through Meerwein-Ponndorf-Verley (MPV) reduction using other alcohols as the H-donors, and homologous aldehyde or ketones is formed after the dehydrogenation of primary or secondary alcohols, respectively [151]. Recently, many researches have been focused on the catalytic transfer hydrogenation (CTH) of LA and its esters to GVL using alcohols as H-donors (Fig. 7). Advances in the production of GVL via CTH are summarized in Table 5 depending on the diversity of H-donors and substrates.

Chia and co-workers have firstly reported the conversion of LA and its esters to GVL through hydrogen transfer from alcohols over inexpensive metal oxide catalysts [152]. Of metal oxides used, ZrO₂ was identified to be the most active catalyst [153] and GVL yields over 80% from alkyl levulinates could be obtained under the optimal reaction conditions. However, a GVL yield of only 22% from LA was observed over ZrO₂ even after long reaction duration of 16 h. The above observation was attributed to the negative impact caused by organic acid because the catalytic activity of catalyst strongly associated with basic sites on ZrO₂ solid [154]. Alkyl levulinates could be readily produced by alcoholysis of carbohydrates with a high yield and be separated economically as compared with LA, because alkyl levulinates such as ML is

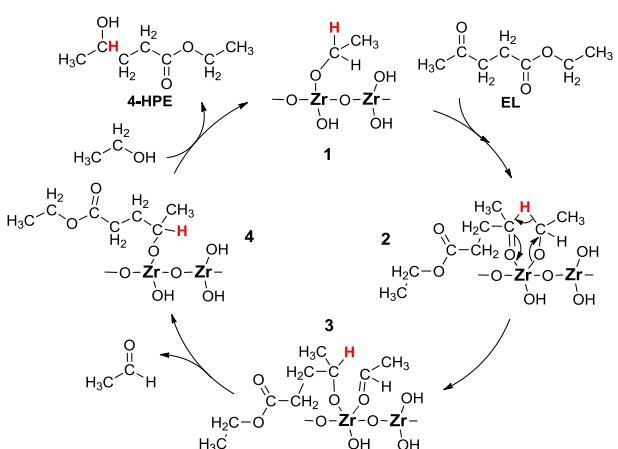


Fig. 7. Proposed mechanism for CTH of EL to GVL using ethanol as H-donor over ZrO(OH)₂ [155].

acid-free and high volatility [22–24]. Therefore, alkyl levulinates, such as ML and EL, are better alternatives than LA for producing GVL from biomass through CTH process.

ZrO(OH)₂ also showed a unexpected catalytic performance for the CTH of levulinates, in contrast to other metal hydroxides including La(OH)₃, Al(OH)₃ and so on [155]. Notably, ZrO(OH)₂ showed a much better catalytic stability than ZrO₂ under the applied reaction conditions. The apparent activation energy for the CTH of EL over Sn(IV) or Zr(IV) zeolite-like catalyst model sites was computed by quantum chemical methods [156]. The calculated apparent activation energy for this transformation over a Sn(IV) zeolite-like catalyst model site (21.9 kcal/mol) was parallel to that (20.7 kcal/mol) catalyzed by Al(III)-isopropoxide (homogeneous catalyst), suggesting that Sn or Zr-based solid catalysts are more favorable for CTH of levulinates to GVL via MPV reduction. Moreover, MPV reduction is strongly associated with the nature of H-donors, and the reduction potential of reducing alcohols decreased in the order of: 2-propanol ≈ 2-butanol < 1-butanol < ethanol < methanol [151,157]. Steric effects of substrates and H-donors should also be taken into account. For instance, the selectivity to GVL from EL or BL in 1-butanol media was lower than that from EL in ethanol media, although 1-butanol has a lower reduction potential than ethanol [155].

Recently, Zr-Beta was prepared and showed high catalytic activity for converting LA to GVL via MPV reduction in 2-pentanol using solvent refluxing method [158]. Zr-Beta was also robust for the vapor phase GVL production (250 °C) via MPV reduction and LA was completely converted under the prescribed conditions. The outstanding performance of Zr-Beta was attributed to the presence of Lewis acidic sites with moderate strength. Besides using LA and its esters as the feedstock, Bui et al. have reported a one-pot approach for the transformation of furfural into GVL through domino reaction catalyzed by zeolites with Brønsted and Lewis acid sites [159]. In this report, Al-MFI-ns (Brønsted acid) and Zr-Beta (Lewis acid) were prepared and catalyzed the alcoholysis of FAL to levulinates, and MPV reduction of furfural and levulinates to FAL and GVL, respectively. This approach gave a best GVL yield of 78% starting from furfural in the presence of Zr-Beta and Al-MFI-ns at 120 °C for 48 h using 2-butanol as solvent and H-donor.

Raney Ni prepared by alkali corrosion of Ni-Al alloy showed a unequaled catalytic performance for the CTH of EL to GVL using 2-propanol as H-donor under room temperature. The best GVL yield of 99% was obtained over Raney Ni at 25 °C for 9 h in 2-propanol media [160]. Differing from the mechanism of MPV reduction, Fu et al. demonstrated that two H-atoms freed from 2-propanol to remain on the Ni surface and then attacked to the carbonyl group in EL. This hydrogenation mechanism is very similar to the hydrogenation of unsaturated compounds under molecular H₂ over Raney Ni. However, γ -hydroxypentanoates, intermediates for the conversion of levulinates to GVL, rather than GVL was verified to be the main product (above 90%) over a commercial Raney Ni catalyst at 25 °C using 2-propanol as the H-donor [90]. GVL yield could be improved to 94% when reaction temperature was increased to 120 °C. It is noted that the Raney Ni catalyst used by Fu et al. was prepared by alkali corrosion of Ni-Al alloy in an aqueous solution of NaOH [160]. Therefore, Geboers et al. proved that residual Al species on the Raney Ni catalyst prepared by alkali corrosion of Ni-Al alloy should be mainly responsible for the lactonization of intermediate γ -hydroxypentanoates to yield GVL at room temperature [90]. For instance, the rate of lactonization of methyl γ -hydroxypentanoate into GVL over γ -Al₂O₃ was much faster than that over Ni/C or Raney Ni.

In addition to the above-mentioned hydrogen sources, LA in aqueous was also completely converted to GVL using syngas (H₂/CO=2:1) as hydrogen source over Au/ZrO₂ at 120 °C for 4 h [161]. At this point, CO and H₂O were converted into H₂ and CO₂ catalyzed by

Table 5

Representative of catalytic systems for producing GVL using alcohols as H-donors.

Catalyst	Substrate	H-donor	T (°C)	t (h)	Yield (%)	Reference
ZrO ₂	LA	2-Butanol	150	16	22	[152]
ZrO ₂	BL	2-Butanol	150	16	84.7	[152]
ZrO ₂	EL	Ethanol	250	3	81.5	[154]
ZrO ₂	EL	2-Propanol	250	1	93.4	[154]
ZrO(OH) ₂	EL	2-Propanol	200	1	88.5	[155]
ZrO(OH) ₂	EL	Ethanol	240	3	78.9	[155]
Zr-Beta	LA	2-Pentanol	118	10	96	[158]
Zr-Beta	LA	2-Pentanol	150	6	82	[158]
Zr-Beta	LA	2-Propanol	250	vapor phase	> 99	[158]
Zr-Beta	ML	2-Butanol	120	5	> 97	[159]
Zr-Beta	LA	2-Butanol	120	11	> 98	[159]
Zr-Beta + Al-MFI-ns	furfural	2-Butanol	120	48	78	[159]
Raney Ni	EL	2-Propanol	25	9	99	[160]
Raney Ni	EL	2-Butanol	25	9	92	[160]

Au/ZrO₂. Xin et al. have developed an electrocatalytic process for converting LA to valeric acid (VA) or GVL [162,163]. This process could give a selectivity of 95 % to VA in acidic electrolyte (pH=0) and 100% selectivity to GVL in neutral electrolyte (pH=7.5). Apparently, this is a very clean and effective process for GVL production from LA. Additionally, several biological processes were also employed for the production of GVL [164,165].

5. Summary and outlook

In this review, we highlight the applications of GVL as a unique solvent for producing chemicals and sugars from biomass and as a promising precursor for new generation biofuels. And, advances in the production of GVL by selective hydrogenation of LA and its esters are also summarized systematically on the basis of the diversity of hydrogen sources.

The future role of GVL will strongly depend on its manufacturing costs from biomass. At some point, a cost-effective process for producing LA from lignocellulosic biomass is the real bottleneck for the GVL production in a large scale. LA could be produced from various biomass materials with high yields [14], however, it is still a challenge to economically separate LA because of its strong acidity and low volatility. Transferring biomass-derived LA/FA into GVL embodies the principle of atom economy and eliminates energy-intensive separation of LA. For example, biomass-derived LA was directly converted to GVL over Au/ZrO₂ or Cu/ZrO₂ catalysts using FA as the in situ hydrogen source [145]. Residual mineral acid catalysts and humins derived from acid-catalyzed degradation of biomass were confirmed to be having a negative impact on the activity of catalysts. Therefore, more studies should be devoted to develop robust and effective catalysts for the conversion of biomass-derived LA against mineral acid catalysts and humins.

On the other hand, the CTH of levulinates via MPV reduction is a better alternative for the production of GVL. For instance, EL could be produced from biomass via ethanolysis [22,24] and be readily separated as its high volatility as compared with LA. Several high-efficiency catalytic strategies for the CTH of pure EL to GVL have been recently developed [155,160]. Compared with conventional hydrogenation route, the management of liquid alcohols used in the CTH route is more convenient than molecular H₂. The CTH of levulinates to GVL can be carried out over cheaper base metal catalysts (containing of Zr, Ni and Sn), facilitating economic feasibility of this approach in a commercial scale. Furthermore, the CTH route via MPV reduction shows an exclusive selectivity to the carbonyl group in EL, avoiding over-hydrogenated products derived from GVL. In particular, the holistic conversion of levulinates to GVL would be largely

promoted under very mild conditions by integrating catalysts for CTH of levulinates to intermediates and subsequent lactonization of intermediates to GVL, respectively [90,160]. It is highly desirable to transfer biomass-derived levulinates (without separation) into GVL using alcohols as in-situ hydrogen source. However, it is a great challenge now that the CTH of biomass-derived levulinates to GVL in the presence of humins, because chewy humins would adsorb onto the surface of catalyst solids and resulted in the deactivation of catalysts. Ongoing researches should be also partially focused on exploring humins-resistant catalysts for GVL production from levulinates derived from alcoholysis of biomass without imputing additional hydrogen source.

Acknowledgments

This work was financially supported by the National Basic Research Program of China, China (2010CB732201), the National High Technology Project (863 project), China (2012AA051802), the Key Research Program from Science and Technology Bureau of Xiamen City, China (3502Z20131016), the National Natural Science Foundation of China, China (21106121), the Key Program for Cooperation Between Universities and Enterprises in Fujian Province, China (2013N5011) and the Fundamental Research Funds for the Xiamen University, China (201312G009).

References

- Perlack RD, Wright LL, Turhollow AF, Graham RL, Stokes BJ, Erbach DC. Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply. DTIC Document; 2005.
- Saxena RC, Adhikari DK, Goyal HB. Biomass-based energy fuel through biochemical routes: a review. Renew Sustainable Energy Rev 2009;13:167–78.
- Röper H. Renewable raw materials in Europe—industrial utilisation of starch and sugar. Starch-Stärke 2002;54:89–99.
- Fischer G, Schrattenholzer L. Global bioenergy potentials through 2050. Biomass Bioenergy 2001;20:151–9.
- Azadi P, Inderwildi OR, Farnood R, King DA. Liquid fuels, hydrogen and chemicals from lignin: a critical review. Renew Sustainable Energy Rev 2013;21:506–23.
- Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass chemistry, catalysts, and engineering. Chem Rev 2006;106:4044–98.
- Li Z, Zeng X, Tang X, Sun Y, Lin L. In-situ-prepared nanocopper-catalyzed hydrogenation-liquefaction of biomass in a glycerol-methanol solvent for biofuel production. Energy Fuels 2014;28:4273–81.
- Demirbaş A. Mechanisms of liquefaction and pyrolysis reactions of biomass. Energy Convers Manag 2000;41:633–46.
- Lin Y, Tanaka S. Ethanol fermentation from biomass resources: current state and prospects. Appl Microbiol Biotechnol 2006;69:627–42.
- Zhang Z, Qiu C, Wetzstein M. Blend-wall economics: Relaxing US ethanol regulations can lead to increased use of fossil fuels. Energy Policy 2010;38:3426–30.

- [11] Zaldivar J, Nielsen J, Olsson L. Fuel ethanol production from lignocellulose: a challenge for metabolic engineering and process integration. *Appl Microbiol Biotechnol* 2001;56:17–34.
- [12] Escobar JC, Lora ES, Venturini OJ, Yáñez EE, Castillo EF, Almazan O. Biofuels: environment, technology and food security. *Renew Sustainable Energy Rev* 2009;13:1275–87.
- [13] Rye L, Blakey S, Wilson CW. Sustainability of supply or the planet: a review of potential drop-in alternative aviation fuels. *Energy Environ Sci* 2010;3:17–27.
- [14] Rackemann DW, Doherty WOS. The conversion of lignocellulosics to levulinic acid. *Biofuel. Bioprod Biorefin* 2011;5:198–214.
- [15] Hu L, Zhao G, Hao W, Tang X, Sun Y, Lin L, et al. Catalytic conversion of biomass-derived carbohydrates into fuels and chemicals via furanic aldehydes. *RSC Adv* 2012;2:11184–206.
- [16] Zhao H, Holladay JE, Brown H, Zhang ZC. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science* 2007;316:1597–600.
- [17] Cai CM, Zhang T, Kumar R, Wyman CE. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. *J Chem Technol Biotechnol* 2014;89:2–10.
- [18] Horváth IT, Mehdi H, Fábos V, Boda L, Mika LT. γ -Valerolactone—a sustainable liquid for energy and carbon-based chemicals. *Green Chem* 2008;10:238–42.
- [19] Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, et al. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour Technol* 2005;96:673–86.
- [20] Girisuta B, LPBM Janssen, Heeres HJ. A kinetic study on the conversion of glucose to levulinic acid. *Chem Eng Res Des* 2006;84:339–49.
- [21] Bozell JJ, Moens L, Elliott DC, Wang Y, Neuenwander GG, Fitzpatrick SW, et al. Production of levulinic acid and use as a platform chemical for derived products. *Resour Conserv Recycl* 2000;28:227–39.
- [22] Peng L, Lin L, Li H, Yang Q. Conversion of carbohydrates biomass into levulinic esters using heterogeneous catalysts. *Appl Energy* 2011;88:4590–6.
- [23] Peng L, Lin L, Li H. Extremely low sulfuric acid catalyst system for synthesis of methyl levulinate from glucose. *Ind Crops Prod* 2012;40:136–44.
- [24] Chang C, Xu G, Jiang X. Production of ethyl levulinate by direct conversion of wheat straw in ethanol media. *Bioresour Technol* 2012;121:93–9.
- [25] Saravananurugan S, Riisager A. Zeolite catalyzed transformation of carbohydrates to alkyl levulimates. *ChemCatChem* 2013;5:1754–7.
- [26] Zhang J, Wu S, Li B, Zhang H. Advances in the catalytic production of valuable levulinic acid derivatives. *ChemCatChem* 2012;4:1230–7.
- [27] Lange JP, van der Heide E, van Buitenen J, Price R. Furfural—a promising platform for lignocellulosic biofuels. *ChemSusChem* 2012;5:150–66.
- [28] Villaverde MM, Bertero NM, Garetto TF, Marchi AJ. Selective liquid-phase hydrogenation of furfural to furfuryl alcohol over Cu-based catalysts. *Catal Today* 2013;213:87–92.
- [29] Lange J-P, van de Graaf WD, Haan RJ. Conversion of furfuryl alcohol into ethyl levulinate using solid acid catalysts. *ChemSusChem* 2009;2:437–41.
- [30] Chen B, Li F, Huang Z, Lu T, Yuan Y, Yuan G. Integrated catalytic process to directly convert furfural to levulinic ester with high selectivity. *ChemSusChem* 2014;7:202–9.
- [31] Neves P, Lima S, Pillinger M, Rocha SM, Rocha J, Valente AA. Conversion of furfuryl alcohol to ethyl levulinate using porous aluminosilicate acid catalysts. *Catal Today* 2013;218:219–76–84.
- [32] Demma Cara P, Ciriminna R, Shiju NR, Rothenberg G, Pagliaro M. Enhanced heterogeneous catalytic conversion of furfuryl alcohol into butyl levulinate. *ChemSusChem* 2014;7:835–40.
- [33] Leitão MLP, Pilcher G, Meng-Yan Y. Enthalpies of combustion of γ -butyrolactone, γ -valerolactone, and δ -valerolactone. *J Chem Thermodyn* 1990;22:885–91.
- [34] Vasiliu M, Guynn K, Dixon DA. Prediction of the thermodynamic properties of key products and intermediates from biomass. *J Phys Chem C* 2011;115:15686–702.
- [35] Martin Alonso D, Wettstein S, Gamma-valerolactone Dumesic J. a sustainable platform molecule derived from lignocellulosic biomass. *Green Chem* 2013;15:584–95.
- [36] Bereczky Á, Lukács K, Farkas M, Dóbé S. Effect of γ -valerolactone blending on engine performance, combustion characteristics and exhaust emissions in a diesel engine. *Nat Resour* 2014;05:177–91.
- [37] Fegyverneki D, Orha L, Láng G, Horváth IT. Gamma-valerolactone-based solvents. *Tetrahedron* 2010;66:1078–81.
- [38] Strádi A, Molnár M, Óvári M, Dibó G, Richter FU, Mika LT. Rhodium-catalyzed hydrogenation of olefins in γ -valerolactone-based ionic liquids. *Green Chem* 2013;15:1857–62.
- [39] Duan Z-Q, Hu F. Highly efficient synthesis of phosphatidylserine in the eco-friendly solvent γ -valerolactone. *Green Chem* 2012;14:1581–3.
- [40] Vance JE, Steenbergen R. Metabolism and functions of phosphatidylserine. *Prog Lipid Res* 2005;44:207–34.
- [41] Qi L, Mui YF, Lo SW, Lui MY, Akien GR, Horváth IT. Catalytic conversion of fructose, glucose, and sucrose to 5-(hydroxymethyl)furfural and/or levulinic and formic acids in gamma-valerolactone as a green solvent. *ACS Catal* 2014;14:70–7.
- [42] Qi L, Horváth IT. Catalytic conversion of fructose to γ -valerolactone in γ -valerolactone. *ACS Catal* 2012;2:2247–9.
- [43] Wettstein S, Martin Alonso D, Chong Y, Dumesic J. Production of levulinic acid and gamma-valerolactone (GVL) from cellulose using GVL as a solvent in biphasic systems. *Energy Environ Sci* 2012;5:8199–203.
- [44] Alonso DM, Gallo JMR, Mellmer MA, Wettstein SG, Dumesic JA. Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts. *Catal Sci Technol* 2013;3:927–31.
- [45] Gurbuz EI, Gallo JM, Alonso DM, Wettstein SG, Lim WY, Dumesic JA. Conversion of hemicellulose into furfural using solid acid catalysts in gamma-valerolactone. *Angew Chem Int Ed* 2013;52:1270–4.
- [46] Zhang L, Yu H, Wang P, Li Y. Production of furfural from xylose, xylan and corncobs in gamma-valerolactone using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst. *Bioresour Technol* 2013;151C:355–60.
- [47] Alonso DM, Wettstein SG, Mellmer MA, Gurbuz EI, Dumesic JA. Integrated conversion of hemicellulose and cellulose from lignocellulosic biomass. *Energy Environ Sci* 2013;6:76–80.
- [48] Luterbacher JS, Rand JM, Alonso DM, Han J, Youngquist JT, Maravelias CT, et al. Nonenzymatic sugar production from biomass using biomass-derived gamma-valerolactone. *Science* 2014;343:277–80.
- [49] Bourne RA, Stevens JG, Ke J, Poliakoff M. Maximising opportunities in supercritical chemistry: the continuous conversion of levulinic acid to gamma-valerolactone in CO_2 . *Chem Commun* 2007;4632–4.
- [50] Hoang TM, Lefferts L, Seshan K. Valorization of humin-based byproducts from biomass processing—a route to sustainable hydrogen. *ChemSusChem* 2013;6:1651–8.
- [51] Bruno TJ, Wolk A, Naydich A. Composition-explicit distillation curves for mixtures of gasoline and diesel fuel with γ -valerolactone. *Energy Fuels* 2010;24:2758–67.
- [52] Du X-L, Bi Q-Y, Liu Y-M, Cao Y, He H-Y, Fan K-N. Tunable copper-catalyzed chemoselective hydrogenolysis of biomass-derived γ -valerolactone into 1,4-pentanediol or 2-methyltetrahydrofuran. *Green Chem* 2012;14:935–9.
- [53] Al-Shaal MG, Dzierbinski A, Palkovits R. Solvent-free γ -valerolactone hydrogenation to 2-methyltetrahydrofuran catalyzed by Ru/C: a reaction network analysis. *Green Chem* 2014;16:1358–64.
- [54] Upare PP, Lee JM, Hwang YK, Hwang DW, Lee JH, Halligudi SB, et al. Direct hydrocyclization of biomass-derived levulinic acid to 2-methyltetrahydrofuran over nanocomposite copper/silica catalysts. *ChemSusChem* 2011;4:1749–52.
- [55] Lange JP, Price R, Ayoub PM, Louis J, Petrus L, Clarke L, et al. Valeric biofuels: a platform of cellulosic transportation fuels. *Angew Chem Int Ed* 2010;49:4479–83.
- [56] Pan T, Deng J, Xu Q, Xu Y, Guo Q, Fu Y. Catalytic conversion of biomass-derived levulinic acid to valerate esters as oxygenated fuels using supported ruthenium catalysts. *Green Chem* 2013;15:2967–74.
- [57] Contino F, Dagaut P, Dayma G, Halter F, Foucher F, Mounaim-Rousselle C. Combustion and emissions characteristics of valeric biofuels in a compression ignition engine. *J Energy Eng* 2014 [http://dx.doi.org/10.1061/\(ASCE\)EY.1943-7897.0000161](http://dx.doi.org/10.1061/(ASCE)EY.1943-7897.0000161) (in press).
- [58] Zeng FX, Liu HF, Deng L, Liao B, Pang H, Guo QX. Ionic-liquid-catalyzed efficient transformation of gamma-valerolactone to methyl 3-pentenoate under mild conditions. *ChemSusChem* 2013;6:600–3.
- [59] Kon K, Onodera W, Shimizu K-i. Selective hydrogenation of levulinic acid to valeric acid and valeric biofuels by a Pt/HMFI catalyst. *Catal Sci Technol* 2014;4:3227–34.
- [60] Chan-Thaw CE, Marelli M, Psaro R, Ravasio N, Zuccheri F. New generation biofuels: γ -valerolactone into valeric esters in one pot. *RSC Adv* 2013;3:1302–6.
- [61] Alonso DM, Bond JQ, Serrano-Ruiz JC, Dumesic JA. Production of liquid hydrocarbon transportation fuels by oligomerization of biomass-derived C9 alkenes. *Green Chem* 2010;12:992–9.
- [62] Bond JQ, Alonso DM, Wang D, West RM, Dumesic JA. Integrated catalytic conversion of γ -valerolactone to liquid alkenes for transportation fuels. *Science* 2010;327:1110–4.
- [63] Bond JQ, Alonso DM, West RM, Dumesic JA. γ -Valerolactone ring-opening and decarboxylation over $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the presence of water. *Langmuir* 2010;26:16291–8.
- [64] Bond JQ, Alonso DM, Wang D, Dumesic JA. Interconversion between γ -valerolactone and pentenoic acid combined with decarboxylation to form butene over silica/alumina. *J Catal* 2011;281:290–9.
- [65] Kellicutt AB, Salary R, Abdelrahman OA, Bond JQ. An examination of the intrinsic activity and stability of various solid acids during the catalytic decarboxylation of γ -valerolactone. *Catal Sci Technol* 2014;4:2267–79.
- [66] Braden DJ, Henao CA, Heltzel J, Maravelias CC, Dumesic JA. Production of liquid hydrocarbon fuels by catalytic conversion of biomass-derived levulinic acid. *Green Chem* 2011;13:1755–65.
- [67] Serrano-Ruiz JC, Wang D, Dumesic JA. Catalytic upgrading of levulinic acid to 5-nonenone. *Green Chem* 2010;12:574–7.
- [68] Serrano-Ruiz JC, Braden DJ, West RM, Dumesic JA. Conversion of cellulose to hydrocarbon fuels by progressive removal of oxygen. *Appl Catal B* 2010;100:184–9.
- [69] Gaertner CA, Serrano-Ruiz JC, Braden DJ, Dumesic JA. Ketonization reactions of carboxylic acids and esters over ceria-zirconia as biomass-upgrading processes. *Ind Eng Chem Res* 2010;49:6027–33.
- [70] Patel AD, Serrano-Ruiz JC, Dumesic JA, Anex RP. Techno-economic analysis of 5-nonenone production from levulinic acid. *Chem Eng J* 2010;160:311–21.
- [71] Oser BL, Carson S, Oser M. Toxicological tests on flavoring matters. *Food Cosmet Toxicol* 1965;3:563–9.
- [72] Cannon GW, Casler Jr. J, Gaines WA. The condensation of γ -butyrolactone and γ -valerolactone with methyl ketones. *J Org Chem* 1952;17:1245–51.
- [73] Mosby WL. The Friedel-Crafts reaction with γ -valerolactone. I. The synthesis of various polymethylnaphthalenes. *J Am Chem Soc* 1952;74:2564–9.

- [74] Mosby WL. Friedel-crafts reactions with γ -valerolactone. II. A synthesis of 1-methyl- and 1, 4-dimethyl-anthracenes. *J Org Chem* 1953;18:964–70.
- [75] Mosby WL. Friedel-crafts reactions with γ -valerolactone. III. Synthesis of a tetramethylphenanthrene. *J Org Chem* 1954;19:294–304.
- [76] Derle SN, Parikh PA. Hydrogenation of levulinic acid and γ -valerolactone: Steps towards biofuels. *Biomass Convers Biorefin* 2014 <http://dx.doi.org/10.1007/s13399-013-0111-5> (in press).
- [77] Pham HN, Pagan-Torres YJ, Serrano-Ruiz JC, Wang D, Dumesic JA, Datye AK. Improved hydrothermal stability of niobia-supported Pd catalysts. *Appl Catal A* 2011;397:153–62.
- [78] Christian Jr RV, Brown HD, Hixon RM. Derivatives of γ -valerolactone, 1,4-pentanediol and 1,4-di-(β -cyanoethoxy)-pentane. *J Am Chem Soc* 1947;69:1961–3.
- [79] Corbel-Demaily L, Ly BK, Minh DP, Tapin B, Espel C, Epron F, et al. Heterogeneous catalytic hydrogenation of biobased levulinic and succinic acids in aqueous solutions. *ChemSusChem* 2013;6:2388–95.
- [80] Li M, Li G, Li N, Wang A-Q, Dong W, Wang X, et al. Aqueous phase hydrogenation of levulinic acid to 1,4-pentanediol. *Chem Commun* 2014;50:1414–6.
- [81] Chalid M, Heeres HJ, Broekhuis AA. Ring-opening of γ -valerolactone with amino compounds. *J Appl Polym Sci* 2012;123:3556–64.
- [82] Zhao Y, Fu Y, Guo Q-X. Production of aromatic hydrocarbons through catalytic pyrolysis of γ -valerolactone from biomass. *Bioresour Technol* 2012;114:740–4.
- [83] Lee CW, Urakawa R, Kimura Y. Copolymerization of γ -valerolactone and β -butyrolactone. *Eur Polym J* 1998;34:117–22.
- [84] Manzer LE. Catalytic synthesis of α -methylene- γ -valerolactone: a biomass-derived acrylic monomer. *Appl Catal A* 2004;272:249–56.
- [85] Lange J-P, Vestering JZ, Haan RJ. Towards 'bio-based' nylon: conversion of γ -valerolactone to methyl pentenoate under catalytic distillation conditions. *Chem Commun* 2007;33:3488–90.
- [86] Raoufnoghdamm S, Rood MT, Buijze FK, Drent E, Bouwman E. Catalytic conversion of gamma-valerolactone to ϵ -caprolactam: towards nylon from renewable feedstock. *ChemSusChem* 2014;7:1984–90.
- [87] Yan Z, Lin L, Liu S. Synthesis of γ -valerolactone by hydrogenation of biomass-derived levulinic acid over Ru/C catalyst. *Energy Fuels* 2009;23:3853–8.
- [88] Chalid M, Broekhuis AA, Heeres HJ. Experimental and kinetic modeling studies on the biphasic hydrogenation of levulinic acid to γ -valerolactone using a homogeneous water-soluble Ru-(TPPTS) catalyst. *J Mol Catal A: Chem* 2011;341:14–21.
- [89] Abdelrahman OA, Heyden A, Bond JQ. Analysis of kinetics and reaction pathways in the aqueous-phase hydrogenation of levulinic acid to form γ -valerolactone over Ru/C. *ACS Catal* 2014;4:1171–81.
- [90] Geboers J, Wang X, ABd Carvalho, Rinaldi R. Densification of biorefinery schemes by H-transfer with Raney Ni and 2-propanol: a case study of a potential avenue for valorization of alkyl levulinates to alkyl γ -hydroxypentanoates and γ -valerolactone. *J Mol Catal A: Chem* 2014;288–289:106–15.
- [91] Upare PP, Lee J-M, Hwang DW, Halligudi SB, Hwang YK, Chang J-S. Selective hydrogenation of levulinic acid to γ -valerolactone over carbon-supported noble metal catalysts. *J Ind Eng Chem* 2011;17:287–92.
- [92] Cao R, Xin J, Zhang Z, Liu Z, Lu X, Ren B, et al. Efficient conversion of α -angelica lactone into γ -valerolactone with ionic liquids at room temperature. *ACS Sustainable Chem Eng* 2014;2:902–9.
- [93] Braca G, Raspolli Galletti AM, Sbrana G. Anionic ruthenium iodocarbonyl complexes as selective dehydroxylation catalysts in aqueous solution. *J Organomet Chem* 1991;417:41–9.
- [94] Starodubtseva EV, Turova OV, Vinogradov MG, Gorshkova LS, Ferapontov VA. Enantioselective hydrogenation of levulinic acid esters in the presence of the Ru(II)-BINAP-HCl catalytic system. *Russ Chem Bull* 2005;54:2374–8.
- [95] Mehdi H, Fábos V, Tuba R, Bodor A, Mika LT, Horváth IT. Integration of homogeneous and heterogeneous catalytic processes for a multi-step conversion of biomass: from sucrose to levulinic acid, γ -valerolactone, 1,4-pentanediol, 2-methyl-tetrahydrofuran, and alkanes. *Top Catal* 2008;48:49–54.
- [96] Delhomme C, Schaper L-A, Zhang-Prefe M, Raudaschl-Sieber G, Weuster-Botz D, Kühn FE. Catalytic hydrogenation of levulinic acid in aqueous phase. *J Organomet Chem* 2013;724:297–9.
- [97] Tukacs JM, Király D, Strádi A, Novodárszki G, Eke Z, Dibó G, et al. Efficient catalytic hydrogenation of levulinic acid: a key step in biomass conversion. *Green Chem* 2012;14:2057–65.
- [98] Li W, Xie J-H, Lin H, Zhou Q-L. Highly efficient hydrogenation of biomass-derived levulinic acid to gamma-valerolactone catalyzed by iridium pincer complexes. *Green Chem* 2012;14:2388–90.
- [99] Deng J, Wang Y, Pan T, Xu Q, Guo QX, Fu Y. Conversion of carbohydrate biomass to gamma-valerolactone by using water-soluble and reusable iridium complexes in acidic aqueous media. *ChemSusChem* 2013;6:1163–7.
- [100] Schuette HA, Thomas RW. Normal valerolactone. III. Its preparation by the catalytic reduction of levulinic acid with hydrogen in the presence of platinum oxide. *J Am Chem Soc* 1930;52:3010–2.
- [101] Kyrides LP, Craver JK. Process for the production of lactones. US: Monsanto Chemicals Company; 1945.
- [102] Dunlop AP, Madden JW. Process of preparing gamma-valerolactone. US: The Quaker Oats Company; 1957.
- [103] Broadbent HS, Campbell GC, Bartley WJ, Johnson JH. Rhenium and its compounds as hydrogenation catalysts. III. Rhenium heptoxide. *J Org Chem* 1959;24:1847–54.
- [104] Yang Y, Gao G, Zhang X, Li F. Facile fabrication of composition-tuned Ru-Ni bimetallics in ordered mesoporous carbon for levulinic acid hydrogenation. *ACS Catal* 2014;4:1419–25.
- [105] Yan K, Chen A. Selective hydrogenation of furfural and levulinic acid to biofuels on the ecofriendly Cu–Fe catalyst. *Fuel* 2013;115:101–8.
- [106] Yan K, Chen A. Efficient hydrogenation of biomass-derived furfural and levulinic acid on the facilely synthesized noble-metal-free Cu–Cr catalyst. *Energy* 2013;58:357–63.
- [107] Yan K, Liao J, Wu X, Xie X. A noble-metal free Cu-catalyst derived hydrotalcite for highly efficient hydrogenation of biomass-derived furfural and levulinic acid. *RSC Adv* 2013;3:3853–6.
- [108] Obregón I, Corro E, Izquierdo U, Requies J, Arias PL. Levulinic acid hydrogenolysis on Al₂O₃-based Ni-Cu bimetallic catalysts. *Chin J Catal* 2014;35:656–62.
- [109] Hengne AM, Rode CV. Cu-ZrO₂ nanocomposite catalyst for selective hydrogenation of levulinic acid and its ester to γ -valerolactone. *Green Chem* 2012;14:1064–72.
- [110] Shimizu K-i, Kanno S, Kon K. Hydrogenation of levulinic acid to γ -valerolactone by Ni and MoO_x co-loaded carbon catalysts. *Green Chem* 16, 2014 3899–3903.
- [111] Zhou H, Song J, Fan H, Zhang B, Yang Y, Hu J, et al. Cobalt catalysts: very efficient for hydrogenation of biomass-derived ethyl levulinate to gamma-valerolactone under mild conditions. *Green Chem* 16, 2014 3870–3875.
- [112] Mohan V, Raghavendra C, Pramod CV, Rajua BD, Rama Rao KS. Ni/H-ZSM-5 as a promising catalyst for vapor phase hydrogenation of levulinic acid at atmospheric pressure. *RSC Adv* 2014;4:9660–8.
- [113] Mohan V, Venkateshwarlu V, Venkata PC, David RB, Rama Rao SK. Vapor phase hydrocyclisation of levulinic acid to γ -valerolactone over supported Ni catalysts. *Catal Sci Technol* 2014;4:1253–9.
- [114] Al-Shaal MG, Wright WRH, Palkovits R. Exploring the ruthenium catalysed synthesis of γ -valerolactone in alcohols and utilisation of mild solvent-free reaction conditions. *Green Chem* 2012;14:1260–3.
- [115] Primo A, Concepcion P, Corma A. Synergy between the metal nanoparticles and the support for the hydrogenation of functionalized carboxylic acids to diols on Ru/TiO₂. *Chem Commun* 2011;47:3613–5.
- [116] Michel C, Zaffran J, Ruppert AM, Matras-Michalska J, Jędrzejczyk M, Grams J, et al. Role of water in metal catalyst performance for ketone hydrogenation: a joint experimental and theoretical study on levulinic acid conversion into gamma-valerolactone. *Chem Commun* 2014, <http://dx.doi.org/10.1039/C4CC04401K> (in press).
- [117] Ortiz-Cervantes C, García JJ. Hydrogenation of levulinic acid to γ -valerolactone using ruthenium nanoparticles. *Inorg Chim Acta* 2013;397:124–8.
- [118] Yan K, Lafleur T, Wu G, Liao J, Ceng C, Xie X. Highly selective production of value-added γ -valerolactone from biomass-derived levulinic acid using the robust Pd nanoparticles. *Appl Catal A* 2013;468:52–8.
- [119] Yan K, Lafleur T, Jarvis C, Wu G. Clean and selective production of γ -valerolactone from biomass-derived levulinic acid catalyzed by recyclable Pd nanoparticle catalyst. *J Clean Prod* 2014;72:230–2.
- [120] Raspolli Galletti AM, Antonetti C, De Luise V, Martinelli M. A sustainable process for the production of γ -valerolactone by hydrogenation of biomass-derived levulinic acid. *Green Chem* 2012;14:688–94.
- [121] Du X, Liu Y, Wang J, Cao Y, Fan K. Catalytic conversion of biomass-derived levulinic acid into γ -valerolactone using iridium nanoparticles supported on carbon nanotubes. *Chin J Catal* 2013;34:993–1001.
- [122] Sudhakar M, Lakshmi Kantam M, Swarna Jaya V, Kishore R, Ramanujachary KV, Venugopal A. Hydroxyapatite as a novel support for Ru in the hydrogenation of levulinic acid to γ -valerolactone. *Catal Commun* 2014;50:101–4.
- [123] Nadgeri JM, Hiyoji N, Yamaguchi A, Sato O, Shirai M. Liquid phase hydrogenation of methyl levulinate over the mixture of supported ruthenium catalyst and zeolite in water. *Appl Catal A* 2014;470:215–20.
- [124] Tukacs JM, Jones RV, Darvas F, Lezsák G, Dibó G, Mika LT. Synthesis of γ -valerolactone using a continuous-flow reactor. *RSC Adv* 2013;3:16283–7.
- [125] Yao Y, Wang Z, Zhao S, Wang D, Wu Z, Zhang M. A stable and effective Ru/polyethersulfone catalyst for levulinic acid hydrogenation to γ -valerolactone in aqueous solution. *Catal Today* 2014;234:245–50.
- [126] Di Mondo D, Ashok D, Waldie F, Schrier N, Morrison M, Schlaf M. Stainless steel as a catalyst for the total deoxygenation of glycerol and levulinic acid in aqueous acidic medium. *ACS Catal* 2011;1:355–64.
- [127] Moreno-Marrodán C, Barbaro P. Energy efficient continuous production of γ -valerolactone by bifunctional metal/acid catalysis in one pot. *Green Chem* 2014;16:3434–8.
- [128] Ye F, Zhang D, Xue T, Wang Y, Guan Y. Enhanced hydrogenation of ethyl levulinate by Pd–AC doped with Nb₂O₅. *Green Chem* 2014;16:3951–7.
- [129] Luo W, Deka U, Beale AM, van Eck ERH, Bruijninx PCA, Weckhuysen BM. Ruthenium-catalyzed hydrogenation of levulinic acid: Influence of the support and solvent on catalyst selectivity and stability. *J Catal* 2013;301:175–86.
- [130] Selva M, Gottardo M, Perosa A. Upgrade of biomass-derived levulinic acid via Ru/C-catalyzed hydrogenation to γ -valerolactone in aqueous-organic-ionic liquids multiphase systems. *ACS Sustainable Chem Eng* 2013;1:180–9.
- [131] Wettstein SG, Bond JQ, Alonso DM, Pham HN, Datye AK, Dumesic JA. RuSn bimetallic catalysts for selective hydrogenation of levulinic acid to γ -valerolactone. *Appl Catal B* 2012;117–118:321–9.
- [132] Alonso DM, Wettstein SG, Bond JQ, Root TW, Dumesic JA. Production of biofuels from cellulose and corn stover using alkylphenol solvents. *ChemSusChem* 2011;4:1078–81.
- [133] Heeres H, Handana R, Chunai D, Borromeus Rasrendra C, Girisuta B, Heeres HJ. Combined dehydration/(transfer)-hydrogenation of C6-sugars (D-glucose and D-fructose) to γ -valerolactone using ruthenium catalysts. *Green Chem* 2009;11:1247–55.

- [134] Ding D, Wang J, Xi J, Liu X, Lu G, Wang Y. High-yield production of levulinic acid from cellulose and its upgrading to γ -valerolactone. *Green Chem* 2014;16:3846–53.
- [135] Raspollì Galletti AM, Antonietti C, Ribechini E, Colombini MP, Nassi o Di Naso N, Bonari E. From giant reed to levulinic acid and gamma-valerolactone: a high yield catalytic route to valeric biofuels. *Appl Energy* 2013;102:157–62.
- [136] Hengne AM, Kamble SB, Rode CV. Single pot conversion of furfuryl alcohol to levulinic esters and γ -valerolactone in presence of sulfonic acid functionized ILs and metal catalysts. *Green Chem* 2013;15:2540–7.
- [137] Johnson TC, Morris DJ, Wills M. Hydrogen generation from formic acid and alcohols using homogeneous catalysts. *Chem Soc Rev* 2010;39:81–8.
- [138] Laurenczy G, Grasemann M. Formic acid as hydrogen source – recent developments and future trends. *Energy Environ Sci* 2012;5:8171–81.
- [139] Shen J, Wyman CE. Hydrochloric acid-catalyzed levulinic acid formation from cellulose: data and kinetic model to maximize yields. *AIChE J* 2012;58:236–46.
- [140] Chang C, Ma XJ, Cen PL. Kinetics of levulinic acid formation from glucose decomposition at high temperature. *Chin J Chem Eng* 2006;14:708–12.
- [141] Kopetzki D, Antonietti M. Transfer hydrogenation of levulinic acid under hydrothermal conditions catalyzed by sulfate as a temperature-switchable base. *Green Chem* 2010;12:656–60.
- [142] Hengne AM, Malawadkar AV, Biradar NS, Rode CV. Surface synergism of Ag-Ni-ZrO₂ nanocomposite for catalytic transfer hydrogenation of bio-derived platform molecules. *RSC Adv* 2013;4:9730–6.
- [143] Deng L, Li J, Lai D-M, Fu Y, Guo Q-X. Catalytic conversion of biomass-derived carbohydrates into γ -valerolactone without using an external H₂ supply. *Angew Chem Int Ed* 2009;48:6529–32.
- [144] Deng L, Zhao Y, Li J, Fu Y, Liao B, Guo Q-X. Conversion of levulinic acid and formic acid into γ -valerolactone over heterogeneous catalysts. *ChemSusChem* 2010;3:1172–5.
- [145] Du X-L, He L, Zhao S, Liu Y-M, Cao Y, He H-Y, et al. Hydrogen-independent reductive transformation of carbohydrate biomass into γ -valerolactone and pyrrolidone derivatives with supported gold catalysts. *Angew Chem Int Ed* 2011;50:7815–9.
- [146] Son PA, Nishimuraa S, Ebitani K. Production of γ -valerolactone from biomass-derived compounds using formic acid as a hydrogen source over supported metal catalysts in water solvent. *RSC Adv* 2014;4:10525–30.
- [147] Yuan J, Li S-S, Yu L, Liu Y-M, Cao Y, He H-Y, et al. Copper-based catalysts for the efficient conversion of carbohydrate biomass into γ -valerolactone in the absence of externally added hydrogen. *Energy Environ Sci* 2013;6:3308–13.
- [148] Fábos V, Míka LT, Horváth IT. Selective conversion of levulinic and formic acids to γ -valerolactone with the Shvo catalyst. *Organometallics* 2014;33:181–7.
- [149] Menashe N, Salant E, Shvo Y. Efficient catalytic reduction of ketones with formic acid and ruthenium complexes. *J Organomet Chem* 1996;514:97–102.
- [150] Du X-L, Bi Q-Y, Liu Y-M, Cao Y, Fan K-N. Conversion of biomass-derived levulinate and formate esters into γ -valerolactone over supported gold catalysts. *ChemSusChem* 2011;4:1838–43.
- [151] de Graauw CF, Peters JA, van Bekkum H, Huskens J. Meerwein-Ponndorf-Verley reductions and oppenauer oxidations an integrated approach. *Synthesis* 1994;10:1007–17.
- [152] Chia M, Dumesic JA. Liquid-phase catalytic transfer hydrogenation and cyclization of levulinic acid and its esters to γ -valerolactone over metal oxide catalysts. *Chem Commun* 2011;47:12233–5.
- [153] Tang X, Sun Y, Zeng X, Hao W, Lin L, Liu S. Novel process for the extraction of ethyl levulinate by toluene with less humins from the ethanolysis products of carbohydrates. *Energy Fuels* 2014;28:4251–5.
- [154] Tang X, Hu L, Sun Y, Zhao G, Hao W, Lin L. Conversion of biomass-derived ethyl levulinate into γ -valerolactone via hydrogen transfer from supercritical ethanol over ZrO₂ catalyst. *RSC Adv* 2013;3:10277–84.
- [155] Tang X, Chen H, Hu L, Hao W, Sun Y, Zeng X, et al. Conversion of biomass to γ -valerolactone by catalytic transfer hydrogenation of ethyl levulinate over metal hydroxides. *Appl Catal B* 2014;147:827–34.
- [156] Assary RS, Curtiss LA, Dumesic JA. Exploring meerwein-ponndorf-verley reduction chemistry for biomass catalysis using a first-principles approach. *ACS Catal* 2013;3:2694–704.
- [157] van der Waal JC, Kunkeler PJ, Tan K, van Bekkum H. Zeolite titanium beta: a selective catalyst for the gas-phase Meerwein-Ponndorf-Verley, and oppenauer reactions. *J Catal* 1998;173:74–83.
- [158] Wang J, Jaenicke S, Chuah G-K. Zirconium-Beta zeolite as a robust catalyst for the transformation of levulinic acid to γ -valerolactone via Meerwein-Ponndorf-Verley reduction. *RSC Adv* 2014;4:13481–9.
- [159] Bui L, Luo H, Gunther WR, Roman-Leshkov Y. Domino reaction catalyzed by zeolites with bronsted and lewis acid sites for the production of gamma-valerolactone from furfural. *Angew Chem Int Ed* 2013;52:8022–5.
- [160] Yang Z, Huang Y-B, Guo Q, Fu Y. Raney Ni catalyzed transfer hydrogenation of levulinate esters to γ -valerolactone at room temperature. *Chem Commun* 2013;49:5328–30.
- [161] Yu L, Du XL, Yuan J, Liu YM, Cao Y, He HY, et al. A versatile aqueous reduction of bio-based carboxylic acids using syngas as a hydrogen source. *ChemSusChem* 2013;6:42–6.
- [162] Xin L, Zhang Z, Qi J, Chadderdon DJ, Qiu Y, Warsko KM, et al. Electricity storage in biofuels: selective electrocatalytic reduction of levulinic acid to valeric acid or gamma-valerolactone. *ChemSusChem* 2013;6:674–86.
- [163] Qiu Y, Xin L, Chadderdon DJ, Qi J, Liang C, Li W. Integrated electrocatalytic processing of levulinic acid and formic acid to produce biofuel intermediate valeric acid. *Green Chem* 2014;16:1305–15.
- [164] Dafoe JT, Daugulis AJ. Production of 4-valerolactone by an equilibrium-limited transformation in a partitioning bioreactor: impact of absorptive polymer properties. *Bioprocess Biosyst Eng* 2013;37:533–42.
- [165] Gotz K, Liese A, Ansorge-Schumacher M, Hilterhaus L. A chemo-enzymatic route to synthesize (S)-gamma-valerolactone from levulinic acid. *Appl Microbiol Biotechnol* 2013;97:3865–73.